

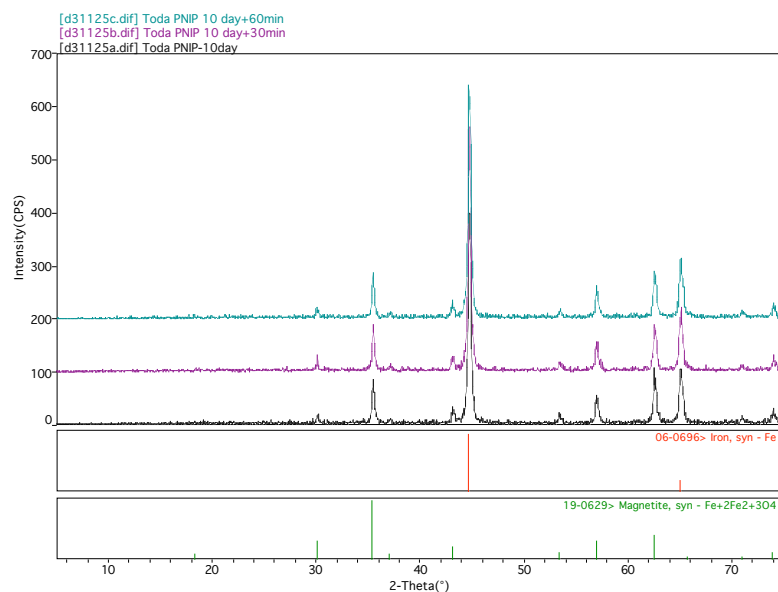
SUPPORTING INFORMATION

Characterization and Properties of Metallic Iron Nanoparticles: Spectroscopy, Electrochemistry, and Kinetics

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- Figure S8. Anodic polarization voltammograms for a stationary powder disk electrode packed with flash-dried $\text{Fe}^{\text{H}2}$ as a function of pre-exposure time to aqueous borate.
- Figure S9. TEMs of $\text{Fe}^{\text{H}2}$ and Fe^{BH} after reaction with benzoquinone.

A.



B.

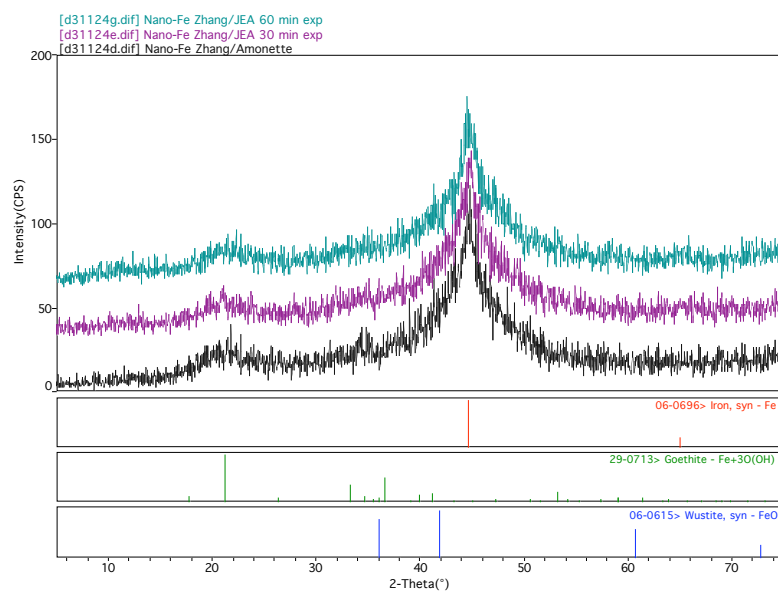
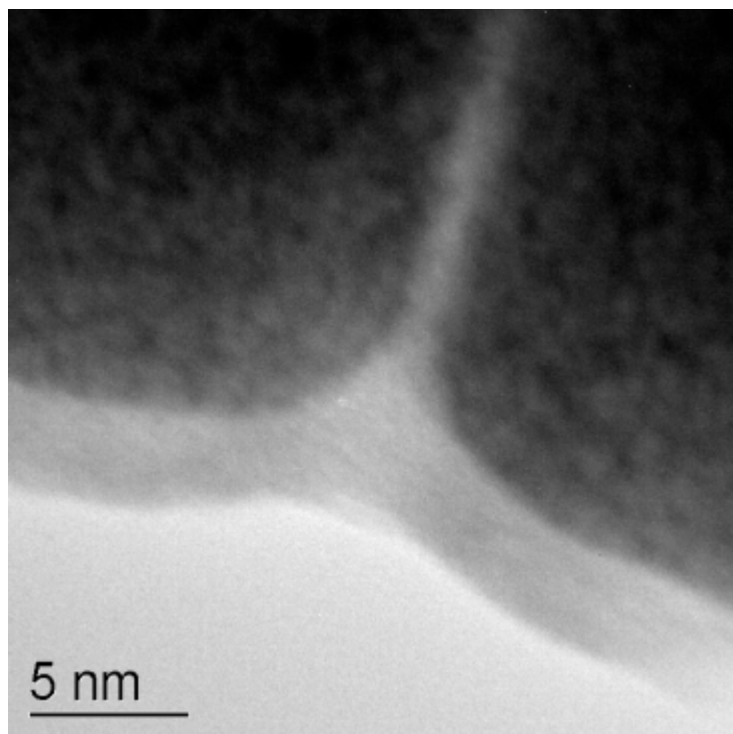


Figure S1. XRD patterns produced from as-received (A) $\text{Fe}^{\text{H}2}$ and (B) Fe^{BH} . The narrow peaks from the $\text{Fe}^{\text{H}2}$ are from both Fe^0 with a 30 nm grain size and magnetite with a 50 nm grain size. The metal-to-oxide ratio in this $\text{Fe}^{\text{H}2}$ sample is about 70% metal and 30% oxide. In other samples the ratio is reversed. The diffraction peaks observed from the Fe^{BH} are from Fe^0 crystallites with an average crystallite or grain size of 1.5 nm.

A.



B.

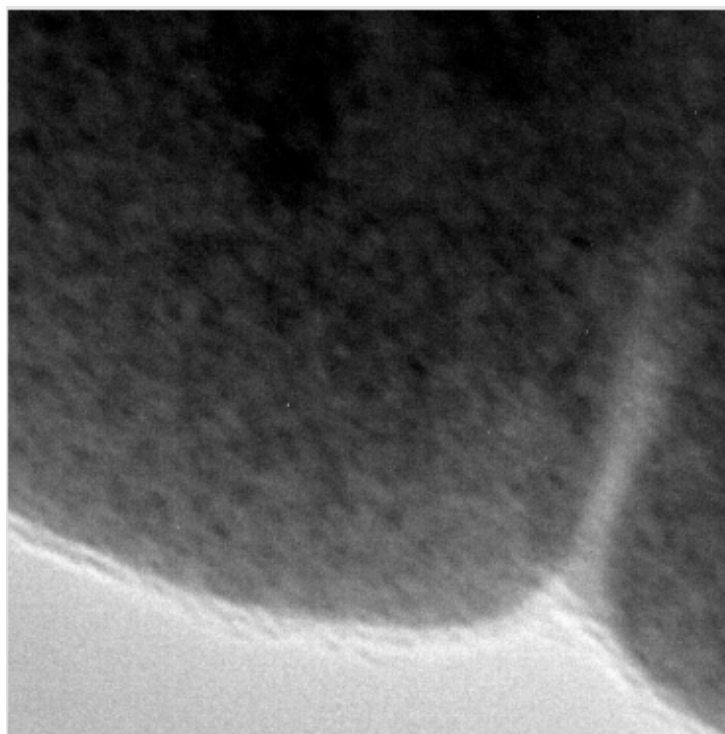


Figure S2. TEMs showing beam damage of shell on Fe^{BH}. Top: image taken as quickly as possible after loading. Bottom: after 1 min exposure to the 200 V electron beam.

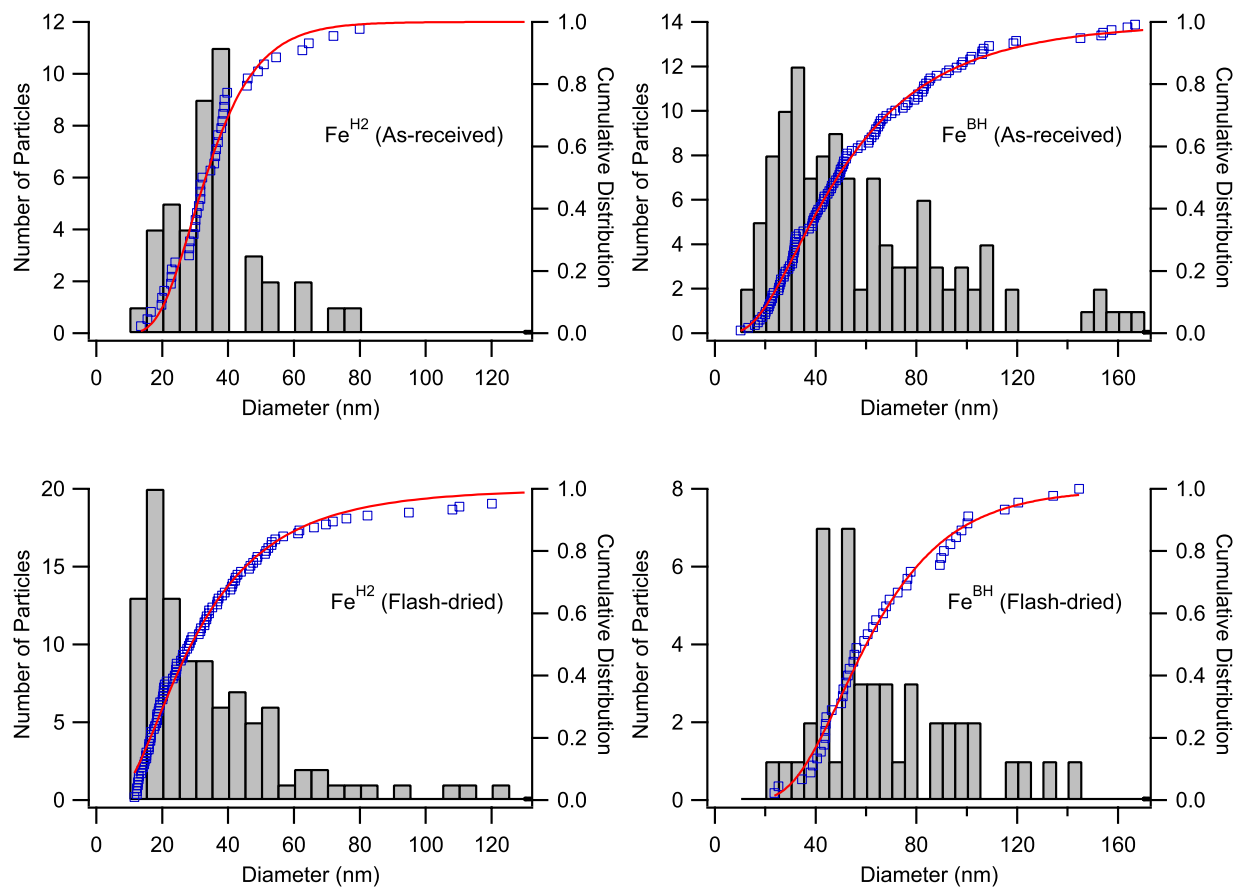
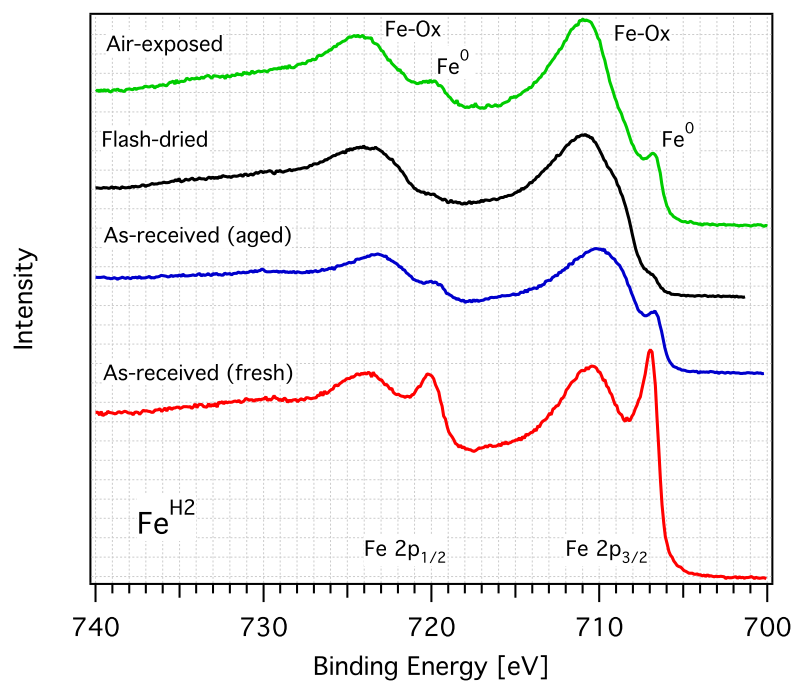


Figure S3. Particle size distributions obtained from TEM. Left axes (number of particles counted) go with the histograms. Right axes (cumulative distribution) go with the squares (individual particles measured) and the solid lines (fits of these data to a log-normal distribution function). In all cases, the log-normal distribution gave a better fit than a normal distribution (not shown).

A.



B.

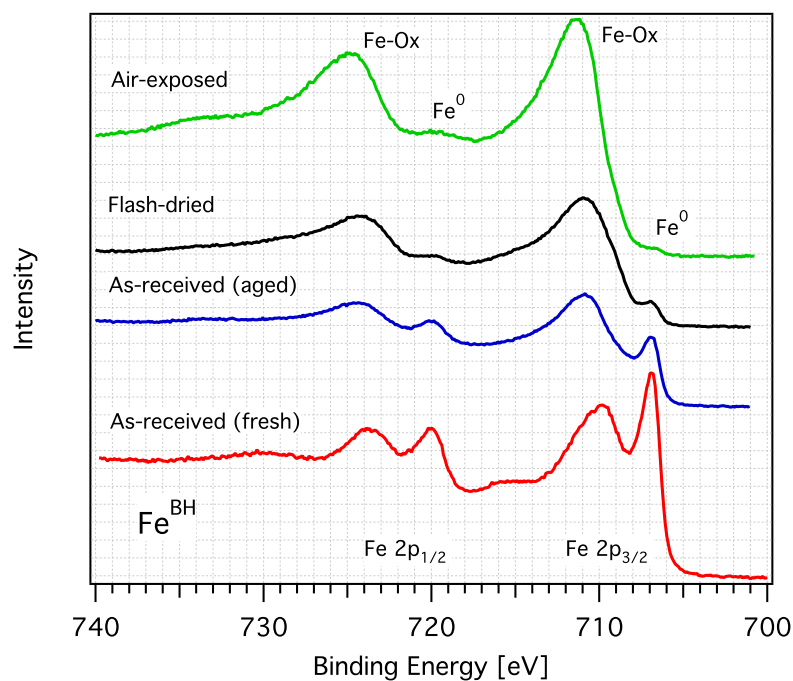


Figure S4. XPS photoemission spectra of the Fe 2p^{3/2} and 2p^{1/2} regions for Fe^{H2} (top) and Fe^{BH} (bottom). Binding energies are scaled to 707.0 eV for Fe⁰. In most cases both metallic (Fe⁰) and oxide states (Fe-Ox) are observed, consistent with an oxide coating on a metallic core.

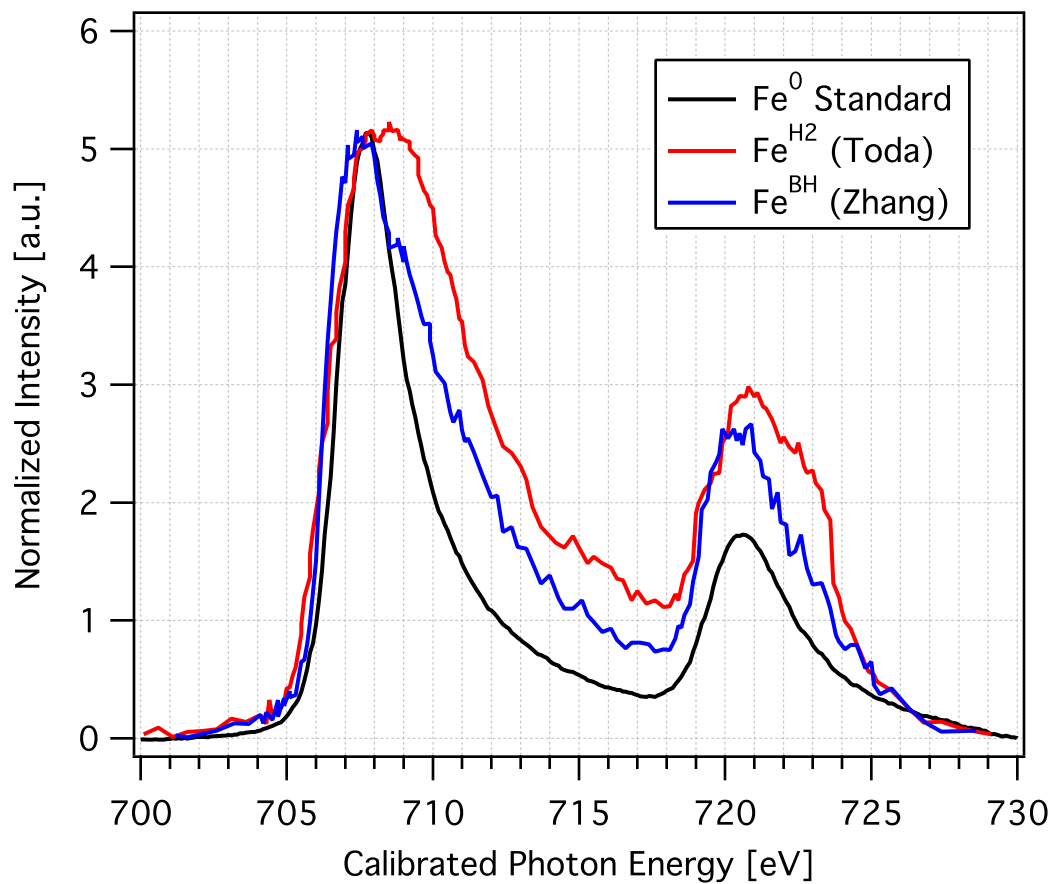


Figure S5. Area averaged L-edge XANES extracted from STXM and TEY (Total Electron Yield) measurements produced from as-received Fe^{BH}, Fe^{H2}, and a Fe⁰ standard. (Fe⁰ standard spectrum provided by T. Droubay).

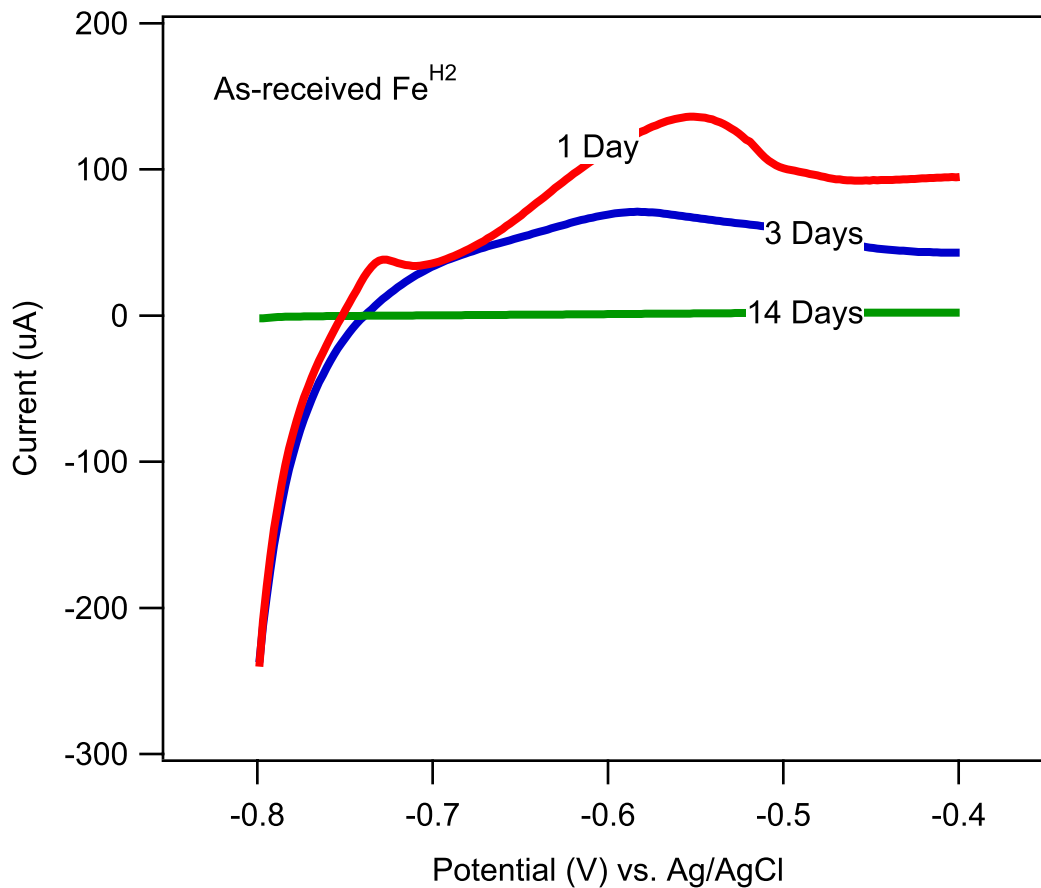


Figure S6. Anodic polarization voltammograms for stationary powder disk electrodes packed with Fe^{H2} that were dried and allowed to age under a glove-box atmosphere. At scan rate = 0.1 mV/s in anaerobic aqueous borate (pH = 8.4).

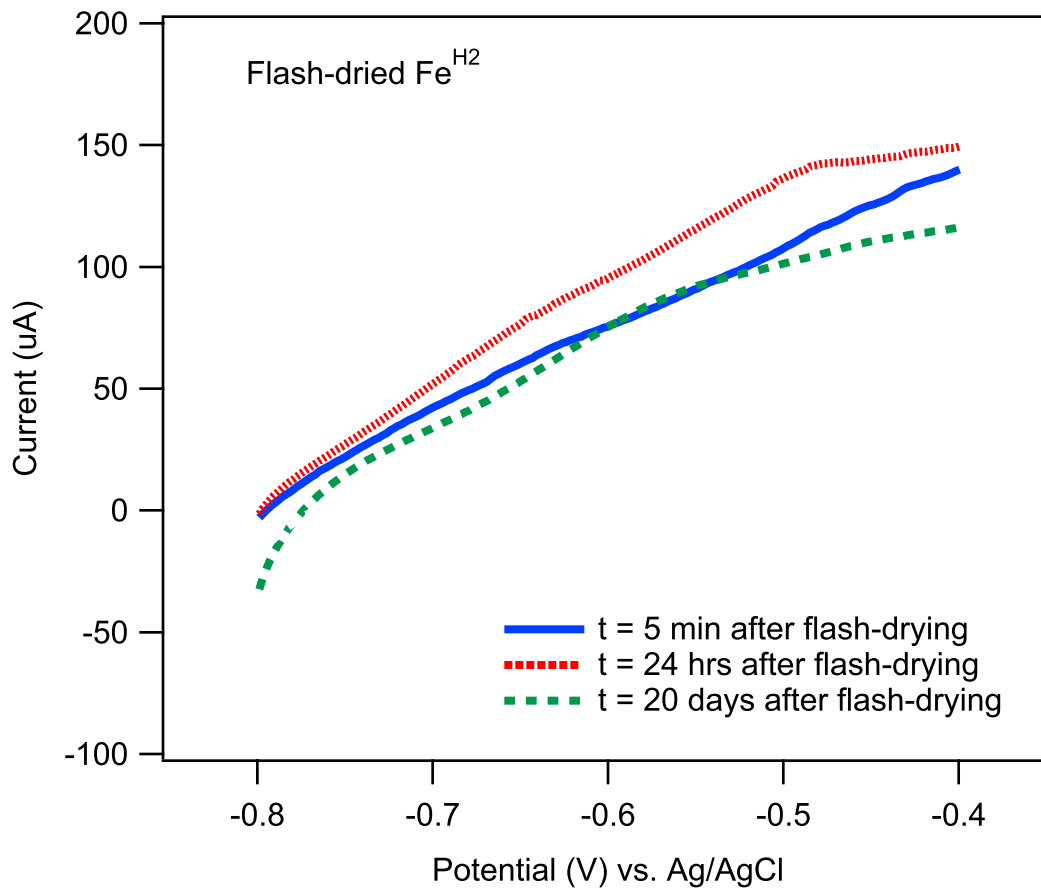


Figure S7. Anodic polarization voltammograms for stationary powder disk electrodes packed with Fe^{H2} that was flash-dried and then aged under a glove-box atmosphere. At scan rate = 0.1 mV/s in anaerobic aqueous borate (pH = 8.4).

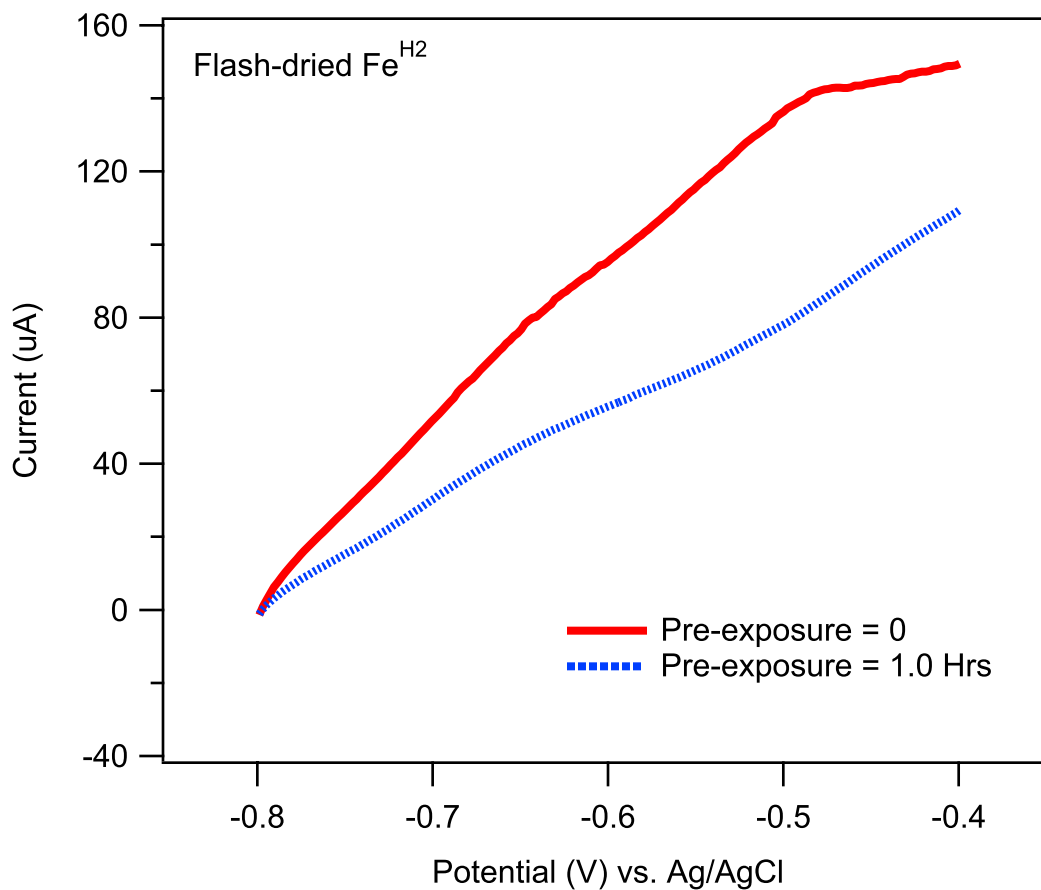


Figure S8. Anodic polarization voltammograms for a stationary powder disk electrode packed with flash-dried Fe^{H2} as a function of pre-exposure time to aqueous borate. At scan rate = 0.1 mV/s in anaerobic aqueous borate (pH = 8.4).

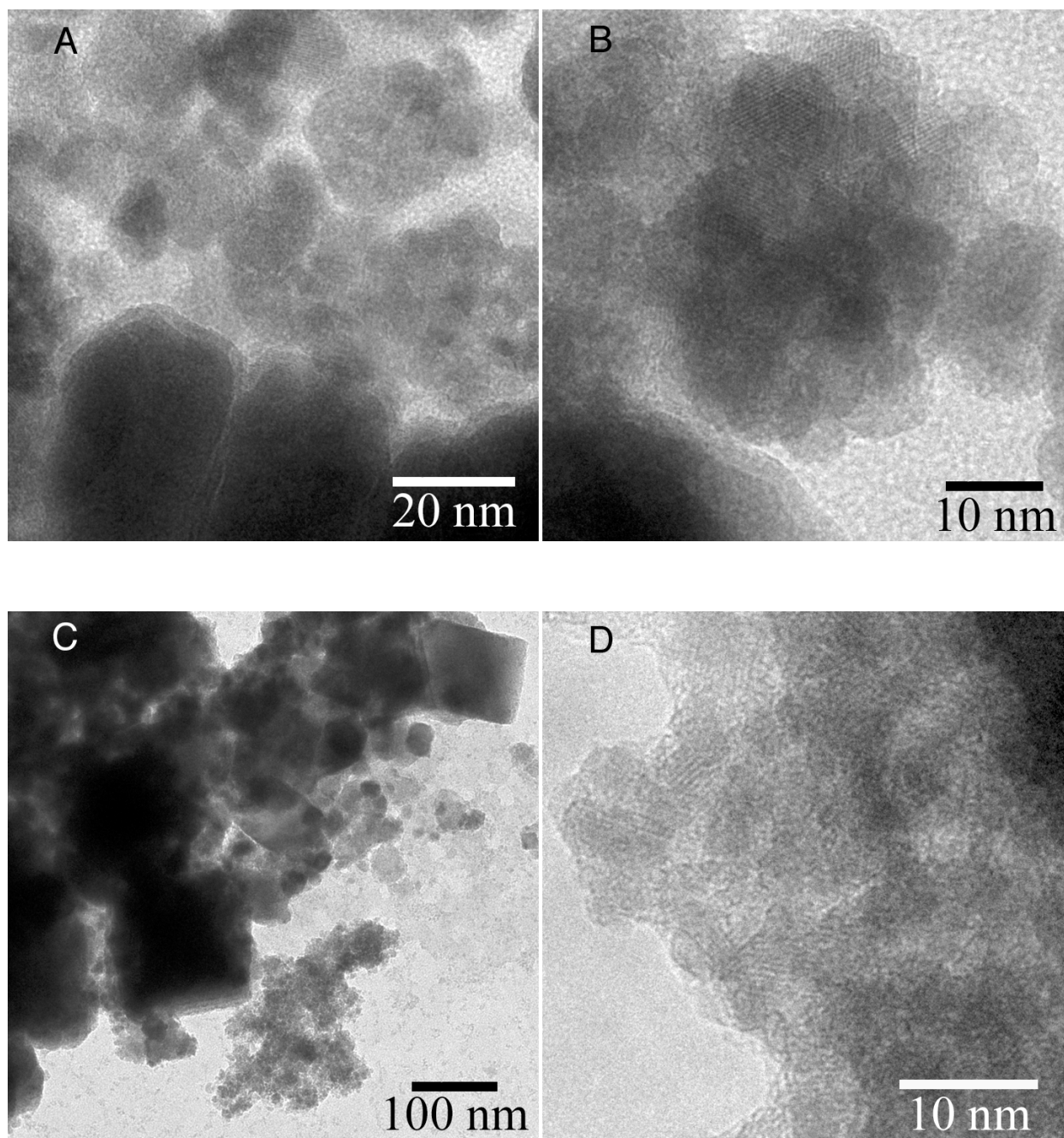


Figure S9. TEMs after reaction with benzoquinone: (A-B) Fe^{BH} , (C-D) of Fe^{H_2} . For both types of iron, two types of material are observed after the reaction: larger particles that appear essentially unaltered, and smaller oxide particles, which are shown at higher magnification in B and D. Diffraction patterns taken from the smaller particles produced from Fe^{BH} are consistent with maghemite/magnetite and goethite and from Fe^{H_2} are consistent with magnetite/maghemite.